

CLAIMS

1. A method for conducting electroplating in the presence of CO<sub>2</sub> and a metal salt-containing aqueous solution, the CO<sub>2</sub> being liquid, subcritical or supercritical, the method further  
5 comprising a step of adding a nonionic compound having a CO<sub>2</sub>-affinitive moiety to a system wherein the aqueous solution and CO<sub>2</sub> coexist, the CO<sub>2</sub>-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of  
10 polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

15 (4) dialkylsiloxo groups.

2. The method according to Claim 1, wherein the nonionic compound is an ether-based or ester-based compound.

20 3. The method according to Claim 1, wherein the nonionic compound is an alcohol-based compound.

4. The method according to Claim 1, wherein the nonionic compound is a fluorinated hydrocarbon.  
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5. The method according to Claim 1, wherein the nonionic compound is a polyalkylsiloxane.

6. The method according to Claim 1, wherein the  
30 nonionic compound is a fluorine-containing polymer.

7. A plating bath comprising a metal salt-containing aqueous solution, CO<sub>2</sub>, and a nonionic compound having a CO<sub>2</sub>-affinitive moiety, the CO<sub>2</sub> being liquid, subcritical or

supercritical, the CO<sub>2</sub>-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

5 (2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

10 (4) dialkylsiloxo groups.

8. An additive for use in electroplating conducted in the presence of liquid, subcritical or supercritical CO<sub>2</sub>, the additive comprising a nonionic compound having a CO<sub>2</sub>-affinitive moiety,

15 the CO<sub>2</sub>-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

20 (2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxo groups.

25 9. A method for preprocessing conducted before plating comprising the step of degreasing and washing a plating substrate prior to plating using a nonionic compound having a CO<sub>2</sub>-affinitive moiety,

30 the CO<sub>2</sub>-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

35 (3) fluorine-containing polyether groups in which some

or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxo groups.

10. A method for postprocessing conducted after plating  
5 comprising the step of washing a plated film after plating using  
a nonionic compound having a CO<sub>2</sub>-affinitive moiety, the CO<sub>2</sub>-  
affinitive moiety being at least one member selected from the  
group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of  
10 polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or  
all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some  
or all of the hydrogen atoms are substituted by fluorine; and

15 (4) dialkylsiloxo groups.

11. A plated film having

(1) per cm<sup>2</sup>, not more than one pinhole having a diameter  
of at least 1 μm;

20 (2) a film thickness of not more than 1 μm; and

(3) a plated film surface roughness of not greater than  
10 nm.

12. The method according to Claim 1, wherein the  
25 nonionic compound used is (CO<sub>2</sub>-affinitive moiety)-X- or X-(CO<sub>2</sub>-  
affinitive moiety)-X- of 1) or 2) below respectively:

1) F-(CF<sub>2</sub>)<sub>q</sub>-(OCF<sub>3</sub>F<sub>6</sub>)<sub>m</sub>-(OC<sub>2</sub>F<sub>4</sub>)<sub>n</sub>-(OCF<sub>2</sub>)<sub>o</sub>-(CH<sub>2</sub>)<sub>p</sub>-X-, or

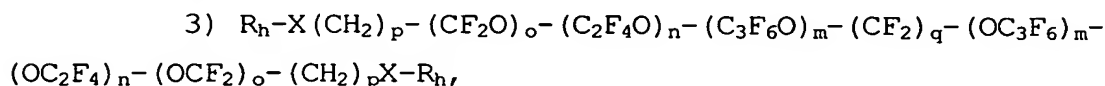
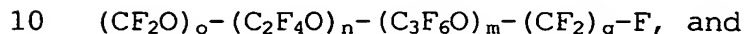
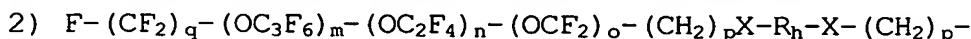
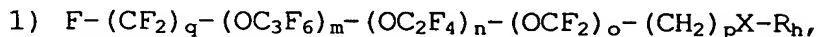
2) -X-(CH<sub>2</sub>)<sub>p</sub>-(CF<sub>2</sub>O)<sub>o</sub>-(C<sub>2</sub>F<sub>4</sub>O)<sub>n</sub>-(C<sub>3</sub>F<sub>6</sub>O)<sub>m</sub>-(CF<sub>2</sub>)<sub>q</sub>-(OC<sub>3</sub>F<sub>6</sub>)<sub>m</sub>-  
(OC<sub>2</sub>F<sub>4</sub>)<sub>n</sub>-(OCF<sub>2</sub>)<sub>o</sub>-(CH<sub>2</sub>)<sub>p</sub>-X-,

30 wherein m, n, o, p, and q are integers not smaller than  
0, m and n are integers from 0 to 15 but not both 0, n + m ≤ 20,  
o = 0 to 20, p = 0 to 2, and q = 1 to 10; the sequence of the  
repeating units not being fixed; -(OC<sub>3</sub>F<sub>6</sub>)<sub>m</sub>- represents -  
(OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>)<sub>m</sub>- or -(OCF(CF<sub>3</sub>)CF<sub>2</sub>)<sub>m</sub>-, and -(OC<sub>2</sub>F<sub>4</sub>)<sub>n</sub>- represents -  
35 (OCF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>- or -(OCF(CF<sub>3</sub>))<sub>n</sub>-, and

each X may be the same or different, and represents a single bond, or O, S, NH, NR ( $R^a$ : alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR<sup>a</sup> ( $R^a$ : alkyl group), NH(O)C, NR(O)C, CH<sub>2</sub>, CHR<sup>a</sup>, CR<sup>a</sup><sub>2</sub> ( $R^a$ : alkyl group), SO<sub>2</sub>NH, or NHSO<sub>2</sub>.

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13. The method according to Claim 1, wherein the nonionic compound is one of 1) to 3):



wherein m, n, o, p, and q are integers not smaller than 0, m and n are integers from 0 to 15 but not both 0,  $n + m \leq 20$ ,  
 15  $o = 0$  to 20,  $p = 0$  to 2, and  $q = 1$  to 10; the sequence of the repeating units not being fixed;  $-(OC_3F_6)_m-$  represents  $-(OCF_2CF_2CF_2)_m-$  or  $-(OCF(CF_3)CF_2)_m-$ , and  $-(OC_2F_4)_n-$  represents  $-(OCF_2CF_2)_n-$  or  $-(OCF(CF_3))_n-$ , and

each X may be the same or different, and represents a  
 20 single bond, or O, S, NH, NR ( $R^a$ : alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR<sup>a</sup> ( $R^a$ : alkyl group), NH(O)C, NR(O)C, CH<sub>2</sub>, CHR<sup>a</sup>, CR<sup>a</sup><sub>2</sub> ( $R^a$ : alkyl group), SO<sub>2</sub>NH, or NHSO<sub>2</sub>, and each R<sub>h</sub> is a hydrophilic moiety and a straight or branched chain hydrocarbon group that may contain hetero atoms.

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14. The method according to Claim 13, wherein R<sub>h</sub> is a polyoxyalkylene group.

15. The method according to Claim 13, wherein the  
 30 nonionic compound comprises a CO<sub>2</sub>-affinitive moiety whose number of carbon atoms is the same as or greater than that of the R<sub>h</sub> group.

16. The method according to Claim 1, wherein the  
 35 nonionic compound comprises (CO<sub>2</sub>-affinitive moiety)-X- or X-(CO<sub>2</sub>-

affinitive moiety)-X- of 1) or 2) below respectively:

1)  $Y-(CF_2)_{m1}-(CH_2)_{n1}-X$ , or

2)  $X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X$ ,

wherein Y is F or H, each X may be the same or  
5 different and represents one member selected from the group  
consisting of COO, O, S, CONH, NHCO, SO<sub>2</sub>NH, and NHSO<sub>2</sub>, m1 is an  
integer from 3 to 20, and each n1 may be the same or different  
and represents an integer from 0 to 2.

10 17. The method according to Claim 16, wherein the  
nonionic compound is one of 1) to 3) below respectively:

1)  $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$ ,

2)  $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-Y$ , or

3)  $R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$ ,

15 wherein Y is F or H, each X may be the same or  
different and represents one member selected from the group  
consisting of COO, O, S, CONH, NHCO, SO<sub>2</sub>NH, and NHSO<sub>2</sub>, each m1 may  
be the same or different and represents an integer from 3 to 20,  
each n1 may be the same or different and represents an integer  
20 from 0 to 2, and each R<sub>h</sub> is a hydrophilic moiety and straight or  
branched chain hydrocarbon group that may contain hetero atoms.

18. The method according to Claim 17, wherein R<sub>h</sub> is a  
polyoxyalkylene group.

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19. The method according to Claim 17, wherein the  
nonionic compound comprises a CO<sub>2</sub>-affinitive moiety whose number  
of carbon atoms is the same as or greater than that of each R<sub>h</sub>  
group.

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